

PATENT SPECIFICATION

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- (21) Application No. 19561/70 (22) Filed 23 April 1970
 (23) Complete Specification filed 19 April 1971
 (44) Complete Specification published 3 Jan. 1974
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 LEYLAND and GWILYM THOMAS JONES



(54) RUBBER POLYESTER COMPOSITIONS

PATENTS ACT 1949

SPECIFICATION NO 1342889

Reference has been directed, in pursuance of Section 8 of the Patents Act 1949, to Specification No 1303138.

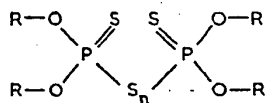
Reference has also been directed, in pursuance of Section 9 subsection (1) of the Patents Act 1949, to Specification No 1271224.

THE PATENT OFFICE
 15 March 1974

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polymeric materials for example in greater strength and durability over rayon and in higher dimensional stability and reduced setting at low temperatures over polyamides, but suffer from the defect of tending to undergo degradation in contact with hot rubber compounds. This degradation is especially severe if the sulphur used in vulcanisation is replaced by sulphur donors such as bis-(morpholino)disulphide in order to improve the ageing characteristics of the vulcanised rubber and minimise reversion during cure. It has now been found that thiophosphoryl polysulphides may be used to replace the sulphur without increasing the tendency of the polyester to degrade.

According to the invention there are provided vulcanisable compositions comprising unvulcanised rubber in contact with polyester material and containing thiophosphoryl polysulphide of the formula:—



wherein each R, which may be the same or

isopropyl, *n*-butyl, isobutyl, cyclohexyl or phenyl group. The preferred value of *n* is 3.

As examples of thiophosphoryl polysulphides which may be used there are mentioned bis(diethylthiophosphoryl)disulphide, bis(diethylthiophosphoryl)trisulphide, bis(diethylthiophosphoryl)tetrasulphide, bis(diisopropylthiophosphoryl)disulphide, bis(di-*n*-butylthiophosphoryl)disulphide, bis(di-*n*-butylthiophosphoryl)trisulphide, bis(di-*n*-butylthiophosphoryl)tetrasulphide, bis(dicyclohexylthiophosphoryl)trisulphide and bis(diphenylthiophosphoryl)trisulphide.

The rubber may be natural or any sulphur-curable synthetic rubber, and includes sulphur-curable polymers such as ethylene/propylene/diolefin copolymers. The use of the thiophosphoryl polysulphides is of especial benefit with natural rubber since the degradation of the polyester is normally more rapid in natural rubber than in synthetic rubbers.

As polyester there is meant a polymer of the type obtainable by condensation of one or more polyfunctional carboxylic acids with one or more polyfunctional alcohols, optionally with the inclusion of minor amounts of other compounds containing two or more active hydrogen atoms such as aminoalcohols, and especially fibre- or film-forming polymers

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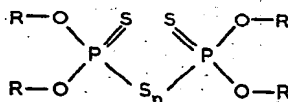
(54) RUBBER POLYESTER COMPOSITIONS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to vulcanisable compositions in which rubber is in contact with polyester materials and more particularly to such compositions which contain thiophosphoryl polysulphides as sulphur donors.

Polymeric materials, especially in the form of fibres, are frequently used in vulcanised rubber compositions as reinforcing agents. Polyesters have some advantages over other polymeric materials for example in greater strength and durability over rayon and in higher dimensional stability and reduced setting at low temperatures over polyamides, but suffer from the defect of tending to undergo degradation in contact with hot rubber compounds. This degradation is especially severe if the sulphur used in vulcanisation is replaced by sulphur donors such as bis-(morpholino)disulphide in order to improve the ageing characteristics of the vulcanised rubber and minimise reversion during cure. It has now been found that thiophosphoryl polysulphides may be used to replace the sulphur without increasing the tendency of the polyester to degrade.

According to the invention there are provided vulcanisable compositions comprising unvulcanised rubber in contact with polyester material and containing thiophosphoryl polysulphide of the formula:—



wherein each R, which may be the same or

different, is an alkyl, alkenyl, cycloalkyl, aryl or aralkyl group and n is 2, 3 or 4.

As examples of groups which may be represented by R there are mentioned alkyl groups such as methyl, ethyl, *n*-propyl, *n*-butyl, isopropyl, *sec*-butyl, isobutyl, *tert*-butyl, amyl, isoamyl, hexyl, heptyl, octyl, 2-ethylhexyl, lauryl and stearyl, alkenyl groups such as allyl, propenyl, 1-butenyl, 1-pentenyl, 1-octenyl and 2-butenyl, cycloalkyl groups such as cyclopentyl, cyclohexyl, methylcyclohexyl, *tert*-butylcyclohexyl, nonylcyclohexyl, 3,3,5-trimethylcyclohexyl, and decalyl, aryl groups such as phenyl, *o*-, *m*-, *p*-tolyl, *α*- and *β*-naphthyl, and aralkyl groups such as benzyl and phenylethyl.

It is preferred that each R be the same. It is preferred that each R be an ethyl, propyl, isopropyl, *n*-butyl, isobutyl, cyclohexyl or phenyl group. The preferred value of n is 3.

As examples of thiophosphoryl polysulphides which may be used there are mentioned bis(diethylthiophosphoryl)disulphide, bis(diethylthiophosphoryl)trisulphide, bis(diethylthiophosphoryl)tetrasulphide, bis(diisopropylthiophosphoryl)disulphide, bis(di-*n*-butylthiophosphoryl)disulphide, bis(di-*n*-butylthiophosphoryl)trisulphide, bis(di-*n*-butylthiophosphoryl)tetrasulphide, bis(dicyclohexylthiophosphoryl)trisulphide and bis(diphenylthiophosphoryl)trisulphide.

The rubber may be natural or any sulphur-curable synthetic rubber, and includes sulphur-curable polymers such as ethylene/propylene/diolefin copolymers. The use of the thiophosphoryl polysulphides is of especial benefit with natural rubber since the degradation of the polyester is normally more rapid in natural rubber than in synthetic rubbers.

As polyester there is meant a polymer of the type obtainable by condensation of one or more polyfunctional carboxylic acids with one or more polyfunctional alcohols, optionally with the inclusion of minor amounts of other compounds containing two or more active hydrogen atoms such as aminoalcohols, and especially fibre- or film-forming polymers

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derived from bifunctional reactants such as terephthalic acid and ethylene glycol. The polyester will normally be in fibre or fabric form but may be in film or other form used to reinforce rubber.

The rubber may contain any of the conventional adjuvants used in rubber technology, for example antioxidants, antiozonants, curing agents, accelerators, retarders, blowing agents, peptising agents, fillers and pigments.

It is preferred in order to increase the rate of cure and impart improved ageing characteristics to the vulcanisate to include a conventional vulcanisation accelerator in the vulcanisable compositions of the invention. As vulcanisation accelerators there may be used any of the well-known types of vulcanisation accelerator, for example thiurams, e.g. tetramethylthiuramdisulphide, thiazoles, e.g. mercaptobenzthiazylidylsulphide, sulphenamides, e.g. mercaptobenzthiazylsulphen(cyclohexyl)-amide, dithiocarbamates, e.g. zinc diethyldithiocarbamate, used singly or in combination.

The unvulcanised rubbers to be used with polyesters to give the vulcanisable composition of the invention may be prepared by incorporating the thiophosphoryl polysulphide and, if used, the accelerator and any other rubber additives into an unvulcanised rubber by any conventional blending procedure, for example on a two-roll mill or in an internal Banbury mixer.

The accelerator may be used in amount up to 4%, and, preferably from 0.1 to 2%, of the weight of rubber.

When used as the sole source of sulphur the thiophosphoryl polysulphide should be present in amount from 0.25 to 5%, and preferably from 0.5 to 3%, of the weight of

rubber.

The thiophosphoryl polysulphide may however be used as only a partial replacement for sulphur, the above ranges of thiophosphoryl polysulphide being used preferably in combination with sulphur in amount not more than 3.0% of the weight of rubber.

The vulcanisable compositions of the invention may be shaped as desired and vulcanised by conventional procedures, i.e. heating to temperatures conveniently between 130 and 200°C.

The vulcanisates obtained from the compositions of the invention are of especial value in the manufacture of tyres, particularly tyres which are intended to be run at sustained high speeds. They are also, however, of value in other rubber/polyester compositions which may be exposed in manufacture or service to elevated temperatures, such as conveyor belting.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight unless otherwise specified.

Example 1.

Rubber mixes of the following compositions are compounded on a two-roll mill. Lengths of polyethylene terephthalate cord are treated with a bonding agent and heat set and are embedded wholly in the mixes and the mixes heated under pressure at 175°C. for 2 hours to cure the rubber and to age the compositions. The cured compositions are then swelled in trichloroethylene for 18 hours, the rubber stripped from the cords, and the breaking strengths of the cords determined. The original breaking strength of the cord is 16 Kg.

Smoked sheet natural rubber	100	100	100	100
High abrasion furnace black	50	50	50	50
Processing oil	6	6	6	6
Zinc oxide	10	10	10	10
Stearic acid	2	2	2	2
Phenyl-β-naphthylamine	1	1	1	1
N-nitrosodiphenylamine	0.5	0.5	0.5	0.5
Benzthiazylsulphenmorpholide	1.0	1.0	1.0	1.0
Sulphur	2.5	1.5	1.5	1.5
Bis(diethylthiophosphoryl)trisulphide	—	0.5	—	—
Bis(diisopropylthiophosphoryl)disulphide	—	—	0.5	—
Bis(morpholino)disulphide	—	—	—	0.5
Breaking strength of polyester after ageing (Kg)	8.4	9.4	9.8	3.9

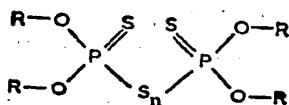
Example 2

The procedure of Example 1 is repeated using rubber mixes described below and a polyethylene terephthalate cord of original breaking strength 16 Kg.

Smoked Sheet natural rubber	100	} in all mixes					
High abrasion furnace black	47.5						
Process oil	3.5						
Zinc oxide	3.0						
Stearic acid	1.0						
Sulphur	2.5	—	—	—	—	—	—
Benzthiazylsulphencyclohexylamide	1	2	—	—	—	1.3	1.3
2,2'-dibenzthiazyldisulphide	—	—	2	—	2	—	—
tetramethylthiuramdisulphide	—	—	—	—	—	0.4	0.4
Bis(diethylthiophosphoryl)trisulphide	—	2	2	3	—	1.3	—
Bis(morpholino)disulphide	—	—	—	—	2	—	1.3
Breaking strength of polyethylene terephthalate (Kg)	9.6	9.9	12.2	13.6	1.2	9.2	1.6

WHAT WE CLAIM IS:—

1. Vulcanisable compositions comprising unvulcanised rubber in contact with polyester material and containing thiophosphoryl polysulphide of the formula:—



wherein each R, which may be the same or different, is an alkyl, alkenyl, cycloalkyl, aryl or aralkyl group and n is 2, 3 or 4.

2. Vulcanisable compositions as claimed in Claim 1 wherein each R is an alkyl group.
 3. Vulcanisable compositions as claimed in Claim 1 wherein each R is an ethyl group.
 4. Vulcanisable compositions as claimed in Claim 1 wherein each R is an isopropyl group.
 5. Vulcanisable compositions as claimed in any of the preceding claims where n is 3.
 6. Vulcanisable compositions as claimed in any of the preceding claims wherein the rubber is a natural rubber.
 7. Vulcanisable compositions as claimed in any of the preceding claims wherein there is

also present a conventional vulcanisation accelerator.

8. Vulcanisable compositions as claimed in Claim 7 wherein the amount of conventional accelerator is up to 4.0% of the weight of rubber.

9. Vulcanisable compositions as claimed in any of the preceding claims wherein the amount of this phosphoryl polysulphide is from 0.25 to 5.0% of the weight of rubber.

10. Vulcanisable compositions as claimed in any of claims 1—8 wherein the amount of thiophosphoryl polysulphide is from 0.5 to 3.0% of the weight of rubber.

11. Vulcanisable compositions as claimed in Claim 9 wherein there is also present sulphur, the amount of sulphur being not more than 3.0% of the weight of rubber, and the thiophosphoryl polysulphide is used as a partial replacement for the sulphur.

12. Vulcanisable compositions as claimed in Claim 1 and substantially as hereinbefore particularly described.

13. Vulcanisates obtained by heating vulcanisable compositions claimed in any of the preceding claims.

H. P. W. HUGGHILL,
Agent for the Applicants.

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